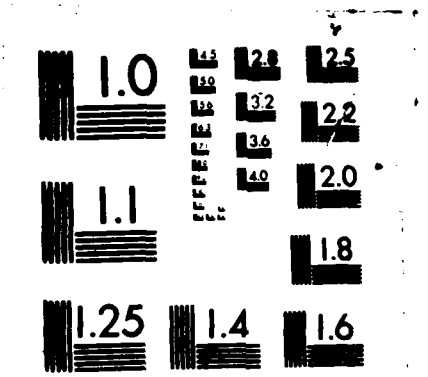
AD-A183 591 A ROTATIONAL ISOMERIC STATE MODEL FOR THE POLYCARBONATE OF 2,2' - BIS (4-H..(U) MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMICAL ENGINEE.. M HUTNIK ET AL. 1/1

UNCLASSIFIED 31 JUL 87 TR-1 N00014-86-K-0768 F/G 7/3 NL



OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0768

R&T Code A400005

Technical Report No. 1

A ROTATIONAL ISOMERIC STATE MODEL FOR THE POLYCARBONATE OF 2,2' - BIS (4-HYDROXYPHENYL) PROPANE

by

Michelle Hutnik and Ulrich W. Suter

Prepared for Publication

in

Polymer Preprints

Massachusetts Institute of Technology

Department of Chemical Engineering

Cambridge, MA 02139

July 31, 1987

A ROTATIONAL ISOMERIC STATE MODEL FOR THE POLYCARBONATE OF 2,2'-BIS(4-HYDROXYPHENYL)PROPANE

MICHELLE HUTNIK AND ULRICH W.SUTER

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA

Recently, the conformations of fragments of the polycarbonate of 2,2'-bis(4-hydroxyphenyl)propane (hereafter abbreviated PC) have been the subject of several detailed studies in which quantum chemical[1-3] and molecular mechanics[3,5-7] methods haven been used. The rotational isomeric state (RIS) model for this chain molecule has not been revised accordingly, and Williams and Flory's[8] RIS scheme is usually used unchanged.[9-11] It seems appropriate and timely to incorporate the newer structural and conformational data into a revised RIS model.

Based mainly on the data provided by Bicerano and Clark[6] and Perez and Scaringe[7] we formulate the following RIS model; all torsion angles are zero in the planar ("zig-zag") conformation depicted in Figure 1. Geometric data is collected in Table 1. Statistical weight matrices and the associated sets of torsion angles are shown in Table 2.

The limiting unperturbed mean-square end-to-end distance of PC, calculated with this RIS model, is

$$\lim_{M \to \infty} \langle r^2 \rangle_0 / M = 0.85 \text{ Å}^2 \text{ mol g}^{-1}$$

This compares favorably to the reported experimental values of 0.75 Å^2 mol g^{-1} (light scattering[12]), 0.87 Å^2 mol g^{-1} ($[\eta]$ [12]), and 0.98 Å^2 mol g^{-1} (light scattering[13]).

ACKNOWLEDGEMENT

We gratefully acknowledge financial support of MH by IBM through a Program of Polymer Science and Technology (PPST) Fellowship at MIT, and of UWS by the Bayer Professorship at MIT. We would especially like to thank Drs. Joseph Bicerano, Hayden Clark, and Alan Letton from Dow Chemical Company for providing us with preprints of their work prior to publication, and for many invigorating discussions.

TABLE 1: Geometric Data

Bond Number	"Real" Length, Å	RIS Bond Length, Å
1	1.54	4.30
2	1.54	4.30
*	2.76	(Phenyl rings included in l_1, l_2)
3	1.41	1.41
4	1.33	1.33
5	1.33	1.33
6	1.41	1.41

	Bond Angles, degrees
$\pi - \theta_1$	109.8
$\pi - \theta_3$	117.7
$\pi - \theta_4$	105.8
$\pi - \theta_5$	117.7

TABLE 2: RIS Parameters

At ca. Room Temperature

Bond Number i	(ϕ_i), degrees	U_i
1	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$
2	45, 135, 225, 315	$\begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$
3	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$
4	0, 180	$\begin{bmatrix} 1 & \gamma \\ 1 & \gamma \\ 1 & \gamma \\ 1 & \gamma \end{bmatrix}$
5	0, 180	$\begin{bmatrix} 1 & \gamma \\ 1 & 0 \end{bmatrix}$
6	45, 135, 225, 315	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}$

where $\gamma = \exp(-500/T)$ with T in K.

REFERENCES

(1) Bicerano, J.; Clark, H. A. "Intrachain Rotations in the Polyestercarbonates. 1. Quantum Mechanical Calculations on the Model Molecules 2,2-Diphenylpropane, Diphenylcarbonate, and Phenyl Benzoate," manuscript to be submitted.

(2) Bicerano, J.; Clark, H. A. "Intrachain Rotations in the Polyestercarbonates. 2. Quantum Mechanical Calculations on Large Model Molecules Fully Representing each Phenyl Ring Environment," manuscript to be submitted.

(3) Letton, A.; Fried, J. R.; Welsh, W. J. "Secondary Relaxation Processes in Bisphenol-A Polysulfone," manuscript to be submitted.

(4) Clark, D.T.; Munro, H. S. Polym. Deg. Stab. 1982, 4, 83.

(5) Tonelli, A. E. Macromolecules, 1972, 5, 558.

(6) Sundararajan, P. R. Can. J. Chem. 1985, 63, 103.

(7) Perez, S.; Scaringe, R. P. Macromolecules 1987, 20, 68.

(8) Williams, A. D.; Flory, P. J. J. Polym. Sci.: Part A-2 1968, 6, 1945.

(9) Yoon, D. Y.; Flory, P. J. Polymer Bull. 1981, 4, 693.

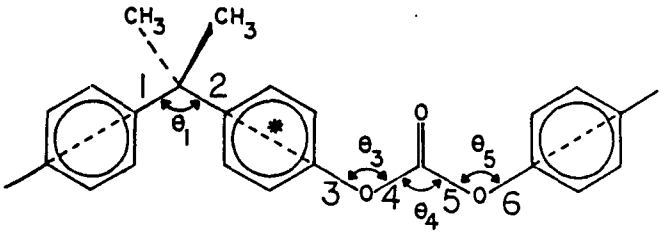
(10) Erman, B.; Marvin, D. C.; Irvine, P. A.; Flory, P. J. Macromolecules 1982, 15, 664.

(11) Erman, B.; Wu, D.; Irvine, P. A.; Marvin, D. C.; Flory, P. J. Macromolecules 1982, 15, 670.

(12) Berry, G. C. J. Chem. Phys. 1967, 46, 1338.

(13) de Chirico, A. Chim. Ind. 1960, 42, 248.

FIGURE 1



DL/1113/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

9-87

DTIC